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The Synthesis of Saturated Cyclic Sulphides

E.N.Karaulova

New syntheses of saturated cyclic sulphides and their functional derivatives are examined. Attention is concentrated on the mode of reaction, the purity of the target products, their yields, and the relation between the structure and properties of cyclic sulphides.
The bibliography includes 142 references.

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I. INTRODUCTION

During the last 10–15 years there has been a sharp growth of the number of studies on the chemistry of organic sulphur compounds. The chemistry of saturated cyclic sulphides has been developing vigorously. They are important models in the study of heteroatomic compounds in petroleum and also serve as the starting materials for the synthesis of polymers, polyfunctional biologically active compounds, and extractants for heavy metals.

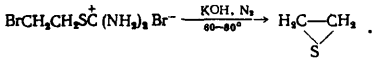
New synthesis of saturated cyclic sulphides during the period 1970–1984 are described in the present review. The yields of the sulphides are indicated (except in those cases where they are not given in the studies quoted or the method of synthesis is not preparative). If reviews or monographs on the relevant topic have been published during the above period, only the most important studies, mainly those published subsequently, are considered.

II. MONOCYCLIC SULPHIDES

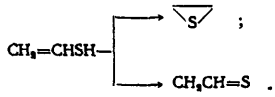
1. Thiirans

The syntheses of thiirans published up to 1976 have been examined in a monograph.[1] The methods of synthesis of thiirans are described systematically in this book in accordance with the types of the ring formation reactions (including the homolytic ring closure via the C=C or C=S bond and heterolytic ring closure as a result of anionotropic or cationotropic transformations). The most important methods of synthesis of thiirans published up to 1980 have been described in a brief review.[2]

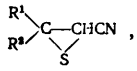
Thiirans have been obtained recently by cyclising *S*-(2-bromoethyl)isothiuronium bromide on heating with aqueous alkali:[3]



It has been shown[4] that up to 30% of thiiran is formed in the synthesis of ethylenethiol from vinyl chloride and hydrogen sulphide in the vapour phase, probably as a result of the isomerisation of ethylenethiol:

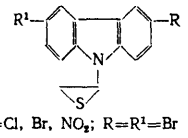


The nitriles of substituted thioglycidic acids



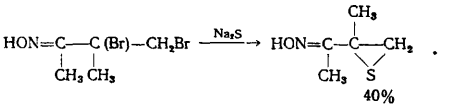
where $R^1 = H$, CH_3, or C_2H_5 and $R^2 = CH_3$ or C_6H_5, have been synthesised[5] by a familiar method involving the condensation of epoxides with potassium thiocyanate; to prevent the desulphurisation of these compounds, it is recommended that the reaction be carried out at pH 6.3–7.

The preparation of carbazolylthiirans with electron-accepting substituents in the carbazole fragment has been described:[6]



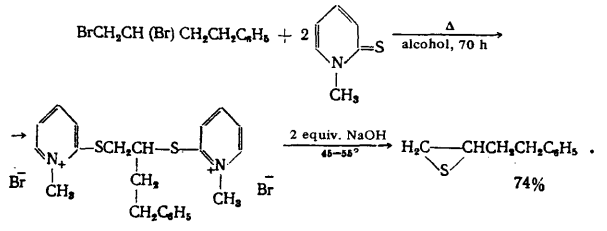
R=H, R¹=Cl, Br, NO_2; R=R¹=Br or $COCH_3$.

It used to be assumed that the interaction of vicinal dihalogenoalkanes with sodium sulphide leads only to polymers.[1] However, it has been possible recently to achieve the synthesis of thiirans from 1,2-dibromoalkanes. When the oxime of 3,4-dibromo-3-methyl-2-butanone was allowed to react with an excess of sodium sulphide in acetone at 20 °C, 2-(α-hydroxyiminoethyl)-2-methylthiiran was obtained:[7]



40%

Japanese chemists[8] proposed a method of synthesis of 2-phenylethylthiacycloalkanes from 1-phenylethyl-ω-dibromoalkanes and *N*-methyl-2(1*H*)-pyridinethione; thus phenylethylthiiran has been obtained from 1-phenylethyl-1,2-dibromethane:

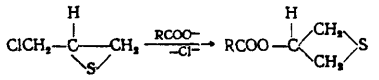


74%

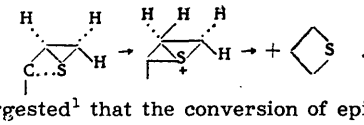
2. Thietans

Certain methods of synthesis of thietans (mainly arylthietans) have been examined in the review by Vedejs and Kraft.[2] Nuretdinova and Arbuzov and co-workers investigated the conditions governing the formation of thiiran and thietan derivatives on treatment of ethylthiohalogenohydrins

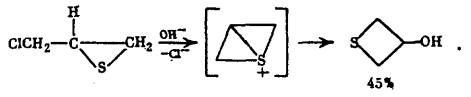
with nucleophiles.[9,10] They found, that, when chloromethylthiiran is treated with sodium and potassium acetates, chloroacetates, methylacrylates, and benzoates in aqueous solutions, 3-acyloxythietans are formed exclusively:



The thiiran–thietan rearrangement then takes place and its mechanism was related by the authors to the formation of an intermediate non-classical thiabicyclobutane cation: the cationotropic transformations of the latter leads, according to Fokin and Kolomiets,[1] to thietan derivatives:

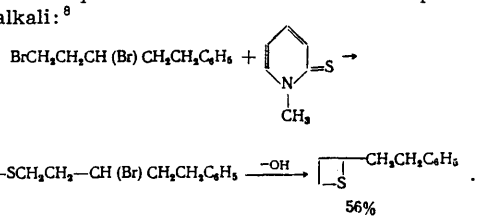


It has been suggested[1] that the conversion of epithiochlorohydrin into 3-hydroxythietan on treatment with aqueous alkali proceeds via the same mechanism:[11]



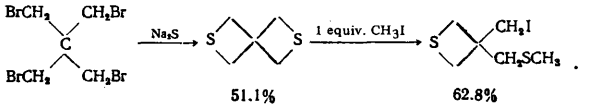
45%

2-Phenylethylthietan can be obtained by prolonged heating of 3,5-dibromo-1-phenylpentane with *N*-methyl-2(1*H*)-pyridinethione and subsequent treatment of the reaction product with aqueous alkali:[8]



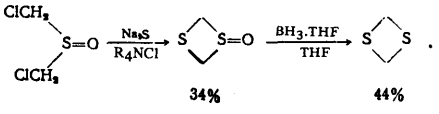
56%

A thietan derivative, namely dithiaspiroheptane, has been synthesised by the cyclocondensation of pentaerythrityl bromide with sodium sulphide in aqueous alcohol; on treatment with methyl iodide, the product is converted into 3-iodomethyl-3-methyl-thiomethylthietan:[12]



51.1% 62.8%

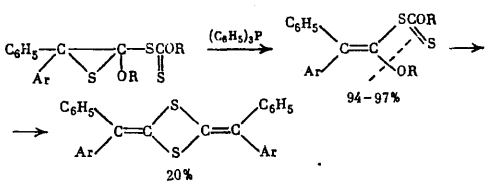
1,3-Diethetan was obtained for the first time in 1982[13] and its properties were investigated. Bis(chloromethyl) sulphoxide cyclises to 1,3-dithietan oxide on treatment with sodium sulphide in an aqueous medium in the presence of a phase transfer catalyst—tricaprilylmethylammonium chloride [the analogous reaction with bis(chloromethyl) sulphide yields only a polymer]. 1,3-Dithietan oxide was reduced to 1,3-dithietan at room temperature by treatment with the borane–tetrahydrofuran complex:



34% 44%

On prolonged storage, 1,3-dithietan is converted into the thioformaldehyde trimer.

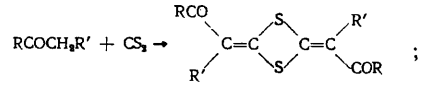
1,3-Dithietan derivatives (thioketen dimers) have been obtained[14] by the mild desulphurisation of 2-acylthio-2-alkoxythiirans by tertiary phosphines and subsequent thermolysis of the thioketenals in accordance with the following scheme:



94–97%

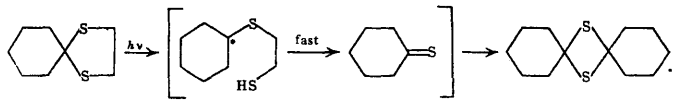
20%

Thioketenal dimers (desaurins) can be obtained in moderate yields by heating carbonyl compounds with carbon disulphide in the presence of potassium hydroxide:[15]

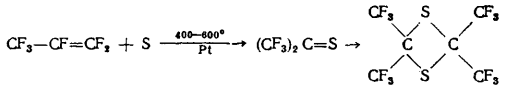


R=C_6H_5, CH_3; R′=H, C_6H_5 .

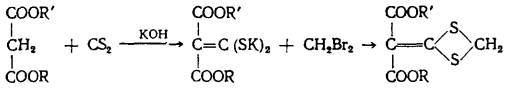
Cyclohexanone thioacetal is converted into spiro-1,3-dithietan on exposure to UV light; the reaction proceeds via a radical mechanism with the intermediate elimination of the radical $\cdot CH_2CH_2SH$ and the formation of cyclohexanethione, which dimerises to spiro-1,3-dithietan:[16]



Hexafluorothioacetone also dimerises to a substituted dithietan:[17]



Dithietanylidenemalonates have been patented as fungicides; it has been recommended that they be obtained by treating malonic acid esters with carbon disulphide in the presence of alkalies; the reaction products are treated with a dihalogenomethane,[18] for example:

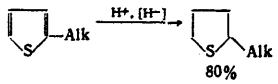


The yields of the required products are 52.8–88%.

3. Thiolans

The syntheses of alkyl- and aryl-thiolans and alkyl- and aryl-thianes, known up to 1969, have been examined in a monograph.[19] Since then new methods of synthesis of the thiolans described previously have been proposed and existing methods have been improved. The purities of the required sulphides have been established by means of gas chromatography and spectroscopic methods. Many thiolans and thianes characterised previously, before the use of these analytical methods, undoubtedly contained considerable admixtures of structural isomers. This must be taken into account in dealing with old data, in particular, with syntheses where dibromoalkanes served as the precursors of thiolans and thianes.

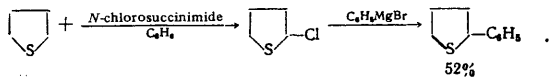
A new method of synthesis of thiolans, including the first member of the series—thiolan itself, involves the ionic hydrogenation of thiophen derivatives.[20] It consists in the successive addition of a proton and hydride ion to the double bonds. Thiophens are acted upon by a trialkylsilane in trifluoroacetic acid:



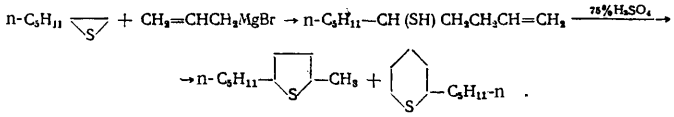
Subsequently the hydrogenating systems were modified[21]—treatment of the corresponding thiophens with the HSi.$(C_2H_5)_3$–HCl/$AlCl_3$ system in methylene chloride produced thiolan, 2-ethylthiolan, 2,5-dimethylthiolan, and, for the first time, 2,5-diphenylthiolan in yields of 25, 80, 75, and 66% respectively. Questions concerning the stereochemistry of disubstituted thiolans were not dealt with by the authors of the above communication.[21]

In order to obtain cyclic sulphides, Crumbie and Ridey[22] hydrolysed alkylthiuronium salts, which is a method widely used previously for the synthesis of alkanethiols. The reaction of 1-chloro-4-iodobutane and one equivalent of thiourea in alcohol yielded 2-(4-chlorobutyl)thiuronium iodide, which was immediately treated with dilute sodium hydroxide. This led to the synthesis of thiolan in 49% yield.

A novel general method of synthesis of 2-substituted cyclic sulphides has been proposed.[23] When unsubstituted cyclic sulphides are chlorinated with *N*-chlorosuccinimide under mild conditions, 2-chlorothiacycloalkanes are formed and are then converted on treatment with methyl- or phenyl-magnesium bromide into 2-substituted thiacycloalkanes (without an admixture of isomers with a different number of members in the ring). 2-Methylthiolan, and for the first time, 2-phenylthiolan were synthesised in this way in satisfactory yields:

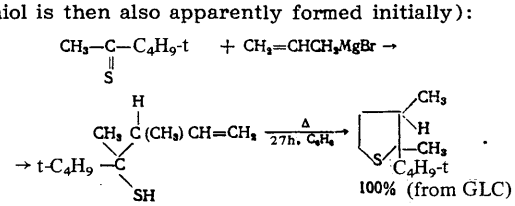


Extremely promising methods of synthesis of thiolans and thianes are based on the cyclisation of unsaturated mercaptans. The use of these reactions makes it possible to develop a general method of synthesis of five- or six-membered cyclic sulphides.[24] The method is based on the interaction of thiirans with allylmagnesium bromide or its homologues, which leads to γδ-unsaturated thiols. Intramolecular cyclisation of the latter via an ionic mechanism leads to sulphides with a five-membered ring and cyclisation via a free-radical mechanism results in the formation of sulphides with six-membered rings; their mixture is usually formed. 2-Methyl-3-n-pentyl- and 2-methyl-3-n-octyl-thiolans,[25] 2-methyl-4-phenylthiolan,[26] and 2-methyl-5-n-pentylthiolan[27] were obtained in accordance with the same scheme for the first time:

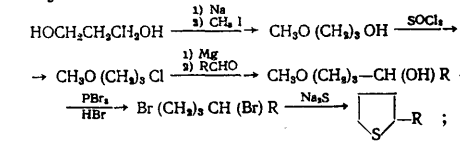


The overall yield of sulphides was 47% and the content of disubstituted thiolans (in the mixture) was 82%.

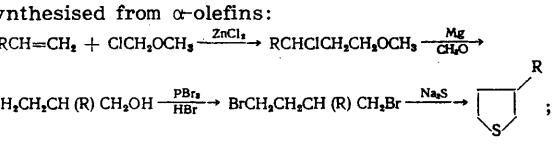
2-t-Butyl-2,3-dimethylthiolan was first synthesised[28] by treating crotyl bromide with t-butyl methyl thione (an unsaturated thiol is then also apparently formed initially):



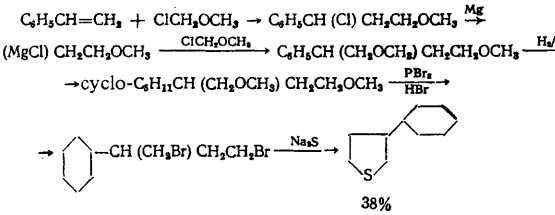
Dibromoalkanes, which are precursors of 2- or 3-substituted thiolans, have been synthesised from chloroalkyl methyl ethers.[29,30] In order to obtain α-substituted 1,4-dibromobutanes, the synthesis was begun with propane-1,3-diol; the substituent was introduced by treating with the corresponding aldehyde the Grignard reagent derived from chloropropyl methyl ether:



The yields of 2-substituted thiolans were 50-80% relative to the dibromides and 27–53% relative to 3-chloropropyl methyl ether. The alkylthiolans obtained in accordance with this scheme contained 17–30% of alkylthianes (with a correspondingly shorter substituent), formed as a result of the cyclisation of the isomeric dibromoalkanes (the bromination method used by the authors leads to a mixture of dibromides which is difficult to resolve). β-Substituted 1,4-dibromobutanes were synthesised from α-olefins:



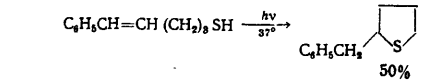
3-n-Butyl- and 3-n-hexyl-thiolans were obtained for the first time. The yields of 3-substituted thiolans (relative to the dibromides) were 64–81%. Volynskii and Shcherbakova[29,30] synthesised for the first time also 3-cyclohexylthiolan using the more readily available styrene rather than vinylcyclohexane:



The 3-methylthiolan obtained in accordance with this scheme was "chromatographically pure", while the remaining 3-substituted thiolans contained, like the 2-substituted derivatives, about 20% of isomeric thianes.

Thiolans obtained by the methods described by Dronov and Krivonogov[27] and Volynskii and Shcherbakova[29] can be separated from the accompanying thianes by preparative gas–liquid chromatography (GLC).

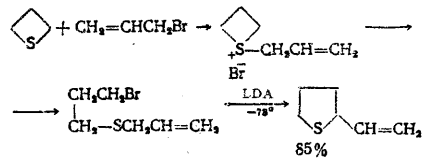
Photolysis of ethylenic mercaptans usually leads to a mixture of two isomeric thiacycloalkanes with different numbers of members in the ring.[31] However, 2-benzylthiolan is formed without an admixture of the isomeric thiane:[31]



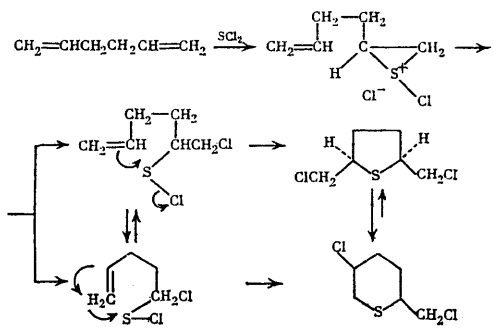
2-Phenylethylthiolan has been obtained[8] in 65% yield from 3,6-dibromo-1-phenylhexane and *N*-methyl-2(1*H*)-pyridinethione analogously to the procedure used for the synthesis of 2-phenylethylthietan described above.

New functional derivatives of thiolan have been obtained both from the corresponding acyclic precursors and by introducing functional groups into thiolans.

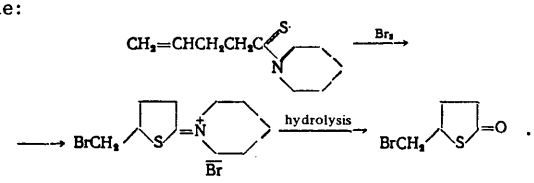
2-Vinylthiolan has been obtained from thietan and allyl bromide.[32] The allylthietanium bromide formed on interaction of these reactants is unstable and rearranges to allyl 3-bromopropyl sulphide, which is converted into 2-vinylthiolan on treatment with lithium diisopropylamide (LDA):



It has been shown recently[33] that, contrary to Lautenschlager's data,[34] the reactions of sulphhr dichloride with hexadiene are not regiospecific. This results in the formation of *cis*-2,5-dichloromethylthiolan and 5-chloro-2-chloromethylthiane (60 : 40). At 20 °C isomerisation takes place gradually and at thermodynamic equilibrium the ratio is 35 : 65 and the overall yield of adducts is 80%. However, they could be separated only after the preliminary oxidation to sulphones (the latter were separated by fractional crystallisation):

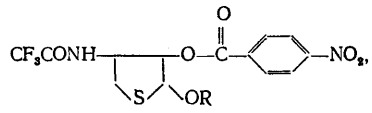


5-Substituted 2-thiolanones are obtained[35] by brominating or iodinating the thioamides of allylacetic acid, which entails heterocyclisation and the formation of halogenomethylpentamethyleneimmoniathiolan halides in yields up to 81%, for example:



The initial thioamides are obtained by refluxing the amides $CH_2 = CHCH_2CH_2CONR_2$ [NR_2 = piperidinyl, morpholinyl, $NHCH_2C_6H_5$, $N(CH_3)_2$, or $NHCH_3$] with P_2S_5 in benzene; it has been established that the "iodocyclisation" reaction is of first order with respect to iodine and thioamides.

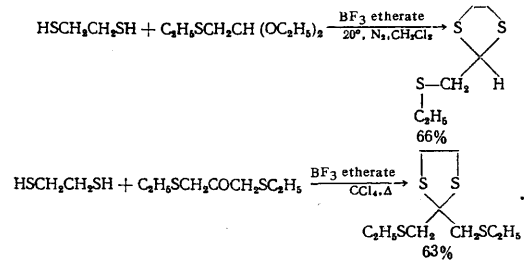
The starting materials for the synthesis of adriamycin analogues, namely the trisubstituted thiolans



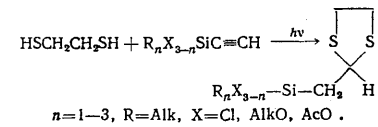
where R = $COCH_3$, $CH(CH_3)_2$, or cyclohexyl, have been obtained[36] from 3,4-dihydroxythiolan by means of successive reduction, trifluoroacylation, esterification, and alkoxylation.

Certain formation reactions of dithiolans and trithiocarbonates, derived from 1,3-dithiolan-2-thiones, have been described in a monograph.[1]

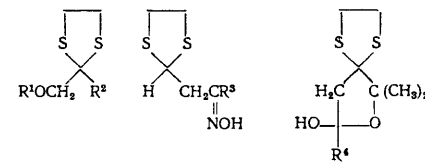
Numerous 2-substituted 1,3-dithiolans have been synthesised in recent years. The heterocycle is usually constructed from ethane-1,2-dithiol. The condensation of this dithiol with the diethylacetal of 2-(ethylthio)acetaldehyde or with 3,7-dithia-5-nonanone yielded 2-(ethylthiomethyl)- and 2,2-di(ethylthiomethyl)-1,3-dithiolan:[37]



2-Silyl-1,3-dithiolans are formed on photochemical interaction of ethane-1,2-dithiol with ethynylsilanes:[38]



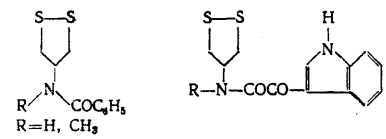
2-Substituted 1,3-dithiolans have been synthesised in order to obtain compounds with fungicidal properties:[39]



R^1=CH_3, CCl_3, C_6H_5, *m*-$C_6H_4NO_2$; R^2=H, CH_2OCH_3, C_6H_5; R^3=C_6H_5, 2-thienyl; R^4 = 2-furyl, 2-thienyl.

Among these compounds, spiro-1,3-dithiolans, especially the compound with R^4 = 2-thienyl, proved to be extremely active against phytophthora on tomatoes.

4-*N*-Acyl-1,2-dithiolans have also been synthesised by the direct acylation of 4-amino-1,2-dithiolans in order to obtain biologically active preparations:[40]



4. Thianes

During the last 15 years many new mono- and poly-alkyl and mono- and poly-aryl-thianes have been synthesised.

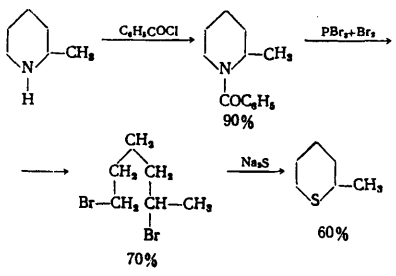
The first member of the series (thiane) has been obtained by two new procedures: in 80% yield from 1-chloro-5-iodopentane and thiourea, analogously to the procedure described above[22] for thiolan, and in 76% yield from ethylene sulphide and allyl-magnesium bromide[41] (in accordance with the procedure proposed a year earlier[24]). Kondo and Negishi[41] directed the cyclisation of the initially formed thiol towards the formation of thianes by the following procedure: magnesium thiolate was decomposed with a solution of ammonium chloride and the resulting unpurified thiol was immediately refluxed in the presence of a radical reaction initiator—azobisisobutyronitrile.

3-Methyl-, 4-methyl- and (for the first time) 4-phenyl-thianes have been obtained in 70—74% yields by an analogous procedure involving the reaction of ethylene sulphide with methylallyl-, crotyl-, or cinnamyl-magnesium bromide.[41] 2-Methyl- and 2,2-dimethyl-thianes have been obtained in 60% yields from allylmagnesium bromide and propylene or isobutylene sulphide.[41] The absence of an admixture of the

isomeric thiolans indicated the selective cleavage of the less sterically hindered C–S bond in the ethylene sulphides.[41]

The mixture containing 75% of 2-n-pentylthiane has been synthesised in 68.7% yield from allylmagnesium bromide and heptene sulphide;[27] the thiane was isolated by GLC (the intermediate decene-5-thiol was cyclised by exposure to UV radiation). 4-n-Pentylthiane (yield 47%) and 4-n-octylthiane (yield 44%) have been obtained analogously from ethylene sulphide and the corresponding alkenylmagnesium bromide, while 3-phenylthiane has been obtained from styrylethylene sulphide and allylmagnesium bromide in ~25% yield.[26]

2-Methyl, 4-methyl-, and 4-t-butyl-thianes have been synthesised from the corresponding alkylpiperidines in accordance with the scheme[42]

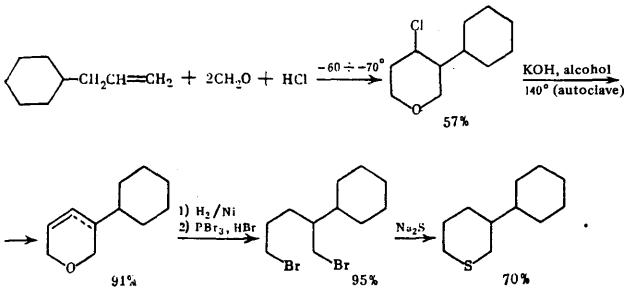


The synthesis includes only three stages (provided of course that alkylpiperidines are available).

2-Methylthiane and (for the first time) 2-phenylthiane have been obtained[23] from thiane in a manner analogous to the above synthesis of 2-phenylthiolan[23] (the yields were respectively 51 and 56%).

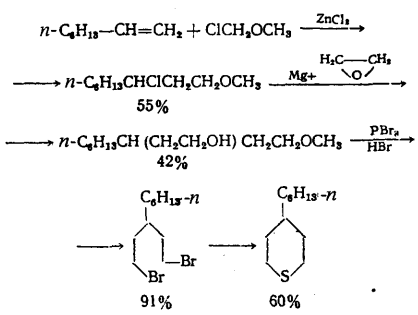
2-Phenylthiane has been synthesised[8] from 3,7-dibromo-1-phenylheptane and *N*-methyl-2(1*H*)-pyridinethione in 40% yield.

1,5-Dibromopentanes, which are precursors of 3- and 4-substituted thianes, have been obtained from α-olefins.[43,44] In order to obtain β-substituted 1,5-dibromopentanes, 3-alkyltetrahydropyrans were initially synthesised by condensing α-olefins with paraformaldehyde:[43]



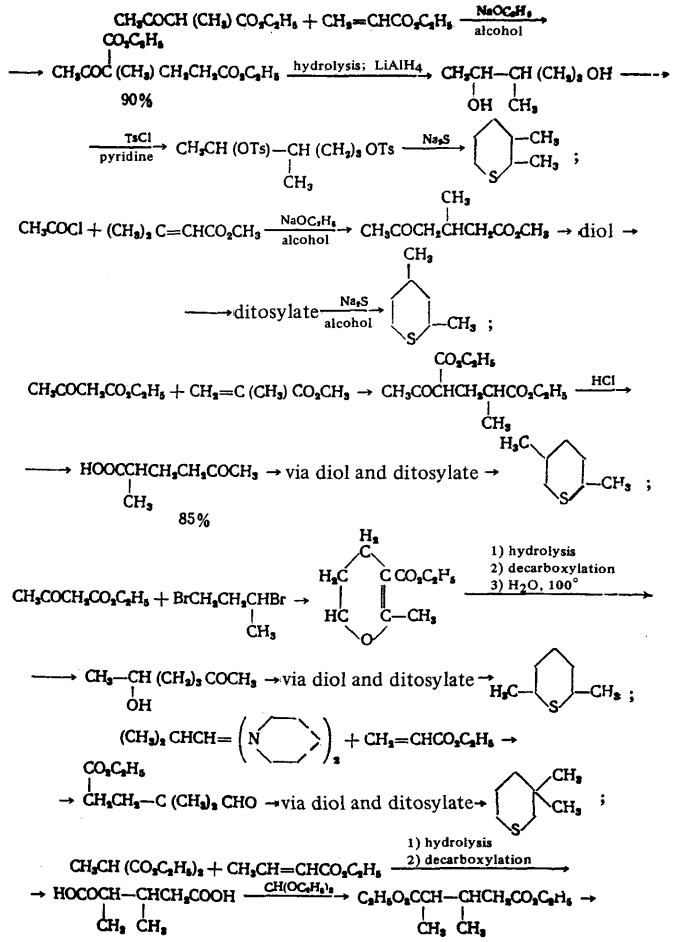
The authors modified the method of the opening of the tetrahydropyran ring having substituted sulphuric acid by phosphorus tribromide. The increase in the cost of the synthesis is compensated by the fact that the yield and purity of the dibromides are then significantly improved. This procedure has been used successfully by the authors in subsequent studies for the cleavage of ethers. 3-n-Butyl-, 3-n-hexyl- and (for the first time) 3-cyclohexyl-thianes were synthesised in accordance with the above scheme[43] in 85, 88, and 70% yields respectively.

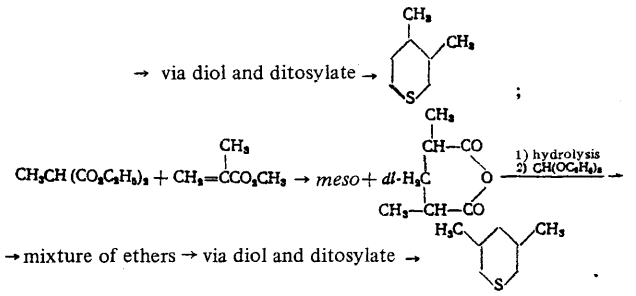
In the synthesis of γ-substituted 1,5-dibromopentanes, carbon chain extension was achieved by two procedures:[44]



Using this method, the authors[44] obtained 4-methyl-, 4n-butyl-, 4n-pentyl-, and 4-phenyl-thianes and also (for the first time) 4n-hexyl- and 4-cyclohexyl-thianes, the yields being respectively 86, 68, 80, 40, 60, and 70%.

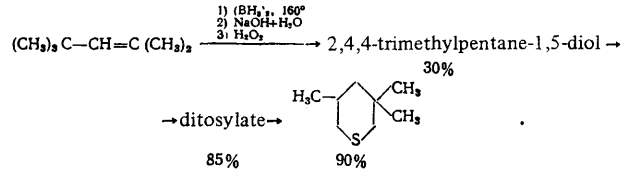
In order to investigate the conformations by ^{13}C NMR, extensive syntheses of dimethylthianes were carried out[42] in 1977; 13 thianes were synthesised for the first time, namely the *cis*- and *trans*-isomers of 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dimethylthianes and 3,3-dimethylthiane. All these compounds are obtained by reducing the corresponding precursors with lithium tetrahydroaluminate to 1,5-diols (90% yields), which were then converted into 1,5-di(toluene-*p*-sulphonate) (yields up to 80%) and their condensation with Na_2S afforded mixtures of the *cis*- and *trans*-substituted dimethylthianes (yields 65–85%). The stereoisomers were separated by preparative GLC. All the precursors of 1,5-diols were obtained from fully available compounds in accordance with the schemes



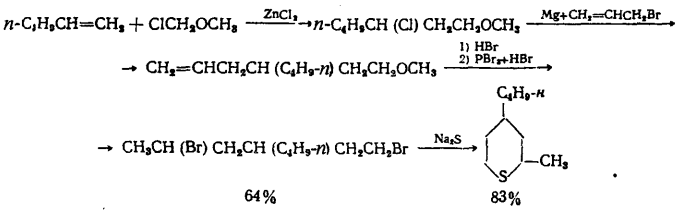


cis-3,5-Dimethylthiane can also be obtained without using preparative GLC: *meso*- and *dl*-dimethylglutaric anhydride are separated by crystallisation, the *meso*-form (yield 25%) is reduced with lithium tetrahydroaluminate to *meso*-2,4-dimethylpentane-1,5-diol and the latter is converted with PBr_3 into the dibromo-derivative (yield 80%), which is treated with Na_2S; the yield of 3,5-dimethylthiane is 75%.

The same workers[42] obtained for the first time 3,3,5-trimethylthiane in accordance with the scheme



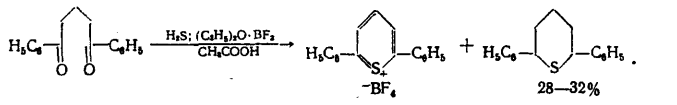
The authors[45] used the scheme proposed previously[44] for the synthesis of 4-substituted thianes in order to obtain 2,4-disubstituted thianes. The growth of the carbon chain, achieved with the aid of allyl bromide, made it possible to introduce a methyl group in the 2-position:



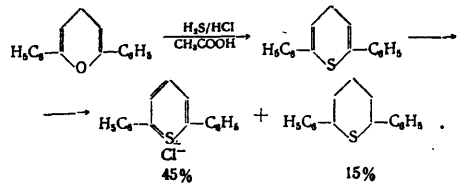
Using this scheme, the authors[45] synthesised for the first time 4-n-butyl-2-methyl-, 2-methyl-4-n-pentyl-, and 2-methyl-4-phenyl-thianes in the form of mixtures of *cis*- and *trans*-isomers (yields 83–87%): the stereoisomers of 2,4-dialkylthianes were separated by GLC. On the other hand, a mixture of the *cis*- and *trans*-2-methyl-4-phenylthianes was oxidised and the resulting mixture of stereoisomeric 1-oxides was separated by fractional crystallisation, after which the 1-oxides were reduced with lithium tetrahydroaluminate to *cis*- and *trans*-2-methyl-4-phenylthianes.[46] Having replaced hydrobromic acid by DBr, the same authors[46] obtained 2-monodeuterio-4-n-butylthiane in 74% yield by means of the same scheme.

2,2-Diphenylthiane was obtained for the first time by hydrogenating *gem*-diphenylthiacyclohexene over 10% Pd/C in a mixture of equal amounts of alcohol and ethyl acetate.[47] Hydrogenation of polyaryl(alkyl)-4*H*-thiopyrans over the same catalyst (in alcohol at 100 °C and a 5% atm hydrogen pressure) led to the corresponding polyaryl(alkyl)thiane—2,6-diphenyl-, 4-methyl-2,6-diphenyl, 2,4,6-triphenyl-, 3,5-dimethyl-2,6-diphenyl-, and 3-methyl-2,4,6-triphenylthianes—in 72–80% yields.[48]

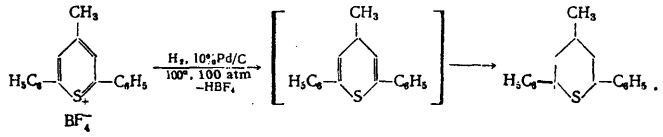
Several further preparative methods of synthesis of 2,6-disubstituted thianes have been proposed,[49,52] for example, from the corresponding 1,5-disubstituted pentane-1,5-diones:[49,50]



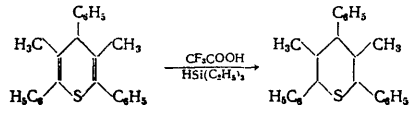
As shown by Kharchenko and Chalaya,[51] 2,6-diphenylthiane is formed as a result of the disproportionation of 2,6-diphenyl-4*H*-thiopyran:



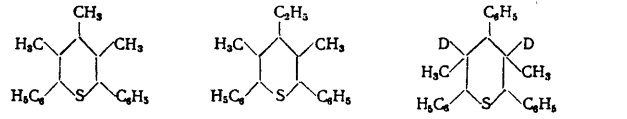
2,6-Diphenylthianes and thiapyrylium salts can be readily separated using their different solubilities in non-polar solvents. Diphenylthianes are also formed smoothly on hydrogenation of thiapyrylium salts[52] (yield 65–79%) with the initial formation of 4*H*-thiopyrans, for example:



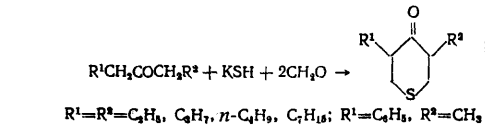
The ionic hydrogenation reaction can be used to obtain thianes from 4*H*-thiopyrans. The corresponding thianes have been obtained from polysubstituted 2,6-diphenyl-4*H*-thiopyrans by treatment with trifluoroacetic acid and an active hydride ion donor—triethylsilane:[53]



The use of CF_3COOD in ionic hydrogenation established that the double bond in 4*H*-thiopyrans is protonated in the C(3)- and C(5)-positions;[53] polysubstituted thianes were obtained for the first time in the above study:[53]



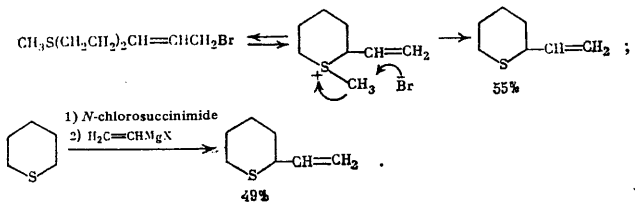
Few functional derivatives of thianes have been synthesised in recent years. A single-stage method of synthesis of disubstituted tetrahydro-1-thiopyran-4-ones has been proposed recently.[54] They were obtained by the thioalkylation reaction—the condensation of ketones containing at the carbonyl group two methylene groups having equal reactivities, with potassium hydrogen sulphide and formaldehyde in alcohol (with brief heating at 50 °C); the yields are 23–72.5%:



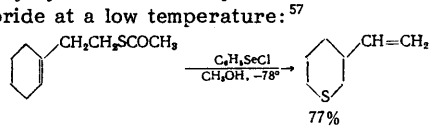
Ketosulphides are mixtures of stereoisomers with the *cis*-isomer predominating slightly; it is recommended that they be used as extractants for palladium ions.

When 6-dimethylamino-5-methylhex-2-en-4-one methiodide is treated with a solution of sodium sulphide at room temperature, 2,5-dimethyl-4-thianone is formed (yield 67%). 2,3-Dimethyl-4-thianone has been obtained analogously (yield 76%).[55]

α-Vinylthiane has been obtained[56] by cyclising 7-bromohept-5-enyl methyl sulphide and also from thiane:

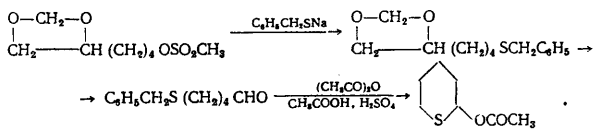


β-Vinylthiane is formed as a result of the cyclisation of acetylthioethylcyclohex-1-ene by treatment with benzeneselenyl chloride at a low temperature:[57]

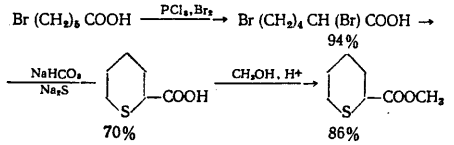


When butyl-lithium and then tetrahydrothiopyran-4-one are added to cyclopentadiene, fulvene—4-cyclopentadienylidenethiane—is formed as an unstable yellow liquid (yield 75%).[58]

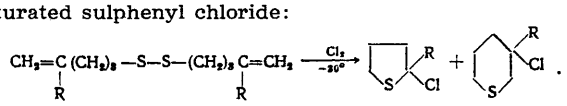
2-Acetoxythiane has been synthesised by a fairly complex procedure:[59] the benzyl derivative was obtained from the methanesulphonate of the formal of hexane-1,2,6-triol and sodium benzylmercaptide and, after hydrolysis and oxidative cleavage, was converted into benzyl 4-formylbutyl sulphide; the latter was subjected to acetolysis in a mixture of acetic anhydride and acetic acid containing sulphuric acid:



There exists yet another method of synthesis of 2-acetoxythiane,[60] but the number of stages is likewise fairly large:

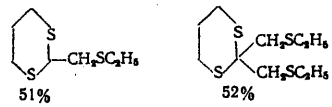


The chlorination of dipent-4-enyl disulphides yields a mixture of α-chlorothiolans and β-chlorothianes; when equilibrium is attained, the thianes predominate.[61] The reaction apparently proceeds via a stage involving the formation of unsaturated sulphenyl chloride:

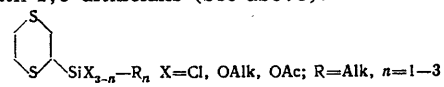


For R = H, the thiolan : thiane ratio is 80 : 20 (under the conditions of kinetic control) or 18 : 82 (under equilibrium conditions); for R = CH_3, the corresponding ratios are 95 : 5 and 4 : 96.

2-(Ethylthiomethyl)- and 2,2-di(ethylthiomethyl)-1,3-dithianes have been synthesised by the reaction of propane-1,3-dithiol with the diethylacetal of 2-ethylthioacetaldehyde or with 3,7-dithia-5-nonanone, analogously to the method described above for 1,3-dithiolans:[37]



The photochemical interaction of ethynylsilanes with ethane-1,2-dithiol results in the formation of 2-silyl-1,4-dithianes together with 1,3-dithiolans (see above):[38]



At −196 °C carbon monosulphide combines with hydrogen chloride to form the chloride of thioformic acid, which is rapidly converted into 2,4,6-trichloro-1,3,5-trithiane in ~50% yield on raising the temperature; 2,4,6-tribromo-1,3,5-trithiane has been obtained analogousiy by reaction with hydrogen bromide in ~75% yield.[62]

Some data on the relations between the structure and properties of the substituted thiolans and thianes. The dependence of the boiling points and retention volumes of alkylthiolans and alkylthianes (including the individual stereoisomers) on the number of substituents and their positions in the ring has been investigated.[63,64] Calculations showed that 2,4-dialkylthianes do not obey the Auwers–Skita rule—the *trans*-isomers have lower boiling points than the *cis*-isomers. Subsequently the applicability of the "reverse" Auwers–Skita rule to 2,4-disubstituted thianes (and to their 1,1-dioxides) was demonstrated experimentally in a number of investigations.[42,45,46]

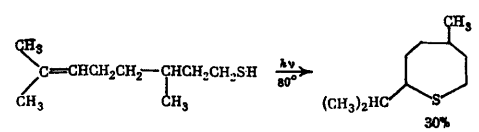
The characteristics of the chemical shift in the ^{13}C NMR spectra of methylthiolans have been examined;[65] the ^{13}C NMR spectra of thiane, twelve of its mono-di, and tri-methyl derivatives, 4-t-butylthiane, and two tetradeuteriothianes have been discussed by Willer and Eliel[42] and those of 1,3-dithianes by Eliel et al.[66] The ratios of the conformers in dimethylthianes and the conformational free energies of the methyl group in the 2-, 3-, and 4-positions in the thiane ring have been determined from the data obtained.

Krapivin and Perepelitchenko[67] investigated the ^{13}C NMR spectra of thianes with long alkyl (C_4–C_5) and aryl substituents and concluded that the steric disposition of substituents in 2,4-disubstituted thianes can be established from the chemical shifts of the ^{13}C nuclei in the 6-position in the thiane ring.

5. Sulphides Containing More Than Six Members in the Ring

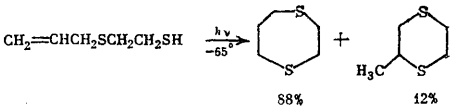
Thiepans have been synthesised by methods analogous to those examined above for thiolans and thianes. Thiepan has been obtained in 34% yield from 1-chloro-6-iodohexane and thiourea.[22] By treating thiepan with *N*-chlorosuccinimide in benzene, Tullen and Bennet[23] obtained α-chlorothiepan and treatment of the latter with methyl- or phenyl-magnesium bromide afforded 2-methylthiepan (yield 66%) and (for the first time) 2-phenylthiepan (yield 56%).

The photochemical cyclisation of 2,6-dimethyloct-2-ene-8-thiol results in the formation of 2-isopropyl-4-methylthiepan without an admixture of the stereoisomeric thiane:[31]



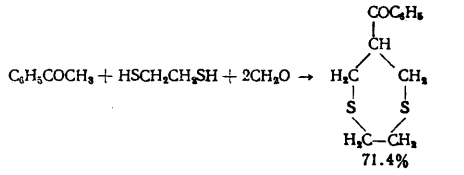
2-Phenylethylthiepan has been synthesised[8] from 3,8-dibromo-1-phenyloctane and *N*-methyl-2(1H)-pyridinethione in 56% yield.

A mixture of isomeric dithiacycloalkanes (overall yield 45%), with the 1,4-dithiepan predominating, is formed when the photochemical cyclisation of allyl 2-mercaptoethyl sulphide is carried out at low temperatures:[31]



2-(Ethylthiomethyl)- and 2,2-di(ethylthiomethyl)-1,3-dithiepans have been obtained from butane-1,4-dithiol by reaction of the latter with the diethylacetal of 2-ethylthioacetaldehyde or 3,7-dithia-5-nonanone respectively.[37]

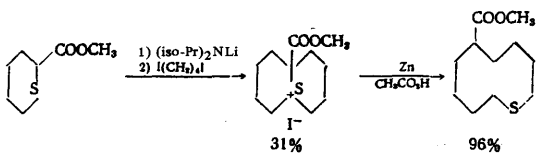
6-Benzoyl-1,4-dithiepan has been synthesised by thioalkylating acetophenone with ethane-1,2-dithiol and formaldehyde in the presence of alkali at room temperature:[68]



Numerous macrocyclic sulphur compounds, namely saturated macrocyclic sulphides, have been synthesised in recent years using noble metals as complex-forming agents and extractants. The methods of synthesis of a wide variety of macrocyclic sulphides, including saturated compounds, published up to 1974, have been examined in the review of Bradshaw and Hui.[69] The results of latter studies (1974–1983) have been very successfully surveyed in two other reviews.[70,71]

A modification of one of the methods of synthesis of macrocyclic sulphides, consisting in the interaction of ω-dihalides with ω-dimercaptans in an alkaline medium at high dilution,[69] merits consideration; instead of the usually employed alkali metal mercaptides, Setzer et al.[72] used a benzyltrimethylammonium salt, which led to a significant increase of the yield of the required products. Under the conditions of high dilution (in absolute methanol), benzyltrimethylammonium, di(2-mercaptoethyl) sulphide, and, simultaneously, 1,2-dibromoethane were made to react whilst heated. 1,4,7-Trithiacyclononane was obtained in 4.4% yield instead of the 0.04% yield obtained previously. Other analogous syntheses have been carried out (the yields expressed as percentages are indicated in brackets): 1,4-dithiepan (65) from ethane-1,2-dithiol and 1,3-dibromopropane; 1,5-dithiacyclooctane (46) from propane-1,3-dithiol and 1,3-dibromopropane; 1,4-dithiacyclooctane (14) from butane-1,4-dithiol and 1,2-dibromoethane; 1,5-dithiacyclononane (9) from the same dithiol and 1,3-dibromopropane; 1,6-dithiacyclodecane (1.5) from the same dithiol and 1,4-dibromobutane. 2-Phenylethylcyclononane has been obtained in 50% yield from 3,10-dibromo-1-phenyldecane and *N*-methyl-2(1*H*)-pyridine thione.[8]

6-Methoxycarbonylthiacyclodecane can be obtained fairly easily from 2-methoxycarbonylthiane via a bicyclic sulphonium salt:[60]



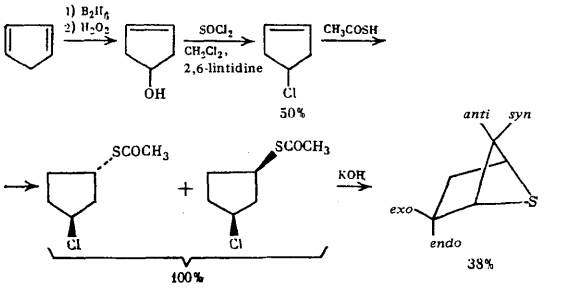
In discussions of the properties of macrocyclic sulphides, it has been noted[69,73] that the melting points of thiacrown ethers increase with increase of the number of sulphur atoms in each analogous series: the larger (compared with oxygen) sulphur atom renders the rings less mobile and the number of conformations in the liquid state and hence the entropy of fusion therefore decrease. Furthermore, the more symmetrical compounds have higher melting points. For the same number of sulphur atoms in the ring, the melting point regularly diminishes as the number of CH_2 groups separating the sulphur atoms rises and very large rings (containing more than 12 members) resemble two parallel chains linked at each end by methylene bridges or a sulphur atom.

III. POLYCYCLIC SULPHIDES

1. Thiabicycloalkanes

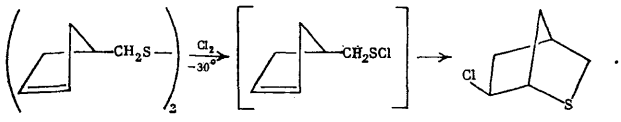
After the methods of synthesis of polycyclic sulphides had been surveyed in a monograph,[19] more than forty new thiabicycloalkanes have been obtained. These are mainly methyl- or phenyl-thiabicyclooctanes and also thiabicyclononanes—both unsubstituted and with methyl or aromatic substituents and thiabicyclodecanes with the same substituents. Most of the methods of synthesis of these compounds have been developed by Soviet workers.

Tabushi et al.[74] obtained the first representative of thiabicyclohexanes—5-thiabicyclo[2.1.1]hexane—from cyclopentadiene in accordance with the scheme

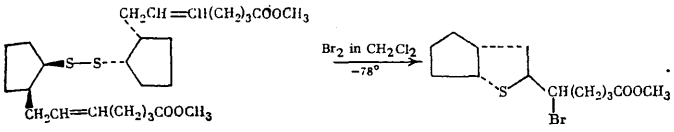


The addition of thioloacetic acid to chlorocyclopentene proceeds quantitatively and leads to a mixture of stereoisomeric 3-acetylthio-1-chlorocyclopentanes. The mixture is added to a boiling aqueous alcoholic solution of potassium hydroxide, whereupon the required product is formed from the *trans*-isomer (it is purified by preparative GLC).

6-*exo*-Chloro-2-thiabicyclo[2.2.1]heptane, its methyl analogue, and 7-*exo*-chloro-2-thiabicyclo[3.2.1]octane are obtained in quantitative yields by the intermolecular cyclisation of sulphenyl chlorides—the intermediates formed on chlorination of unsaturated disulphides at a low temperature:[75]

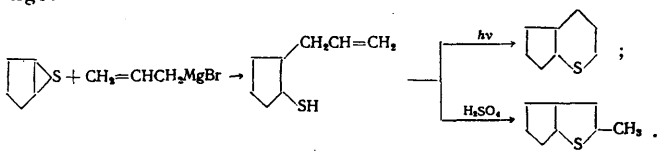


The bromination of substituted dicyclopentyl disulphide proceeds similarly—3-(1-bromo-4-methoxycarbonylbutyl)-2-thiabicyclo[3.3.0]octane has been obtained:[76]

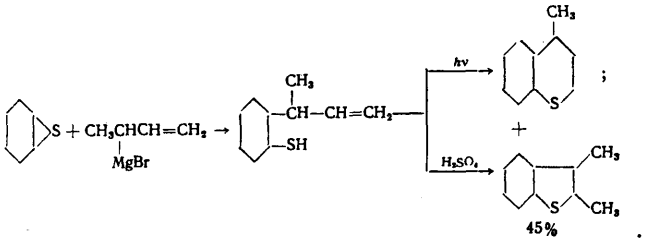


Thiabicyclooctanes, thiabicyclononanes, and thiabicyclodecanes have been synthesised successfully by condensing cycloalkene sulphides with allylmagnesium bromide and its derivatives. The reaction proceeds analogously to that examined above for thiolans and thianes.[24]

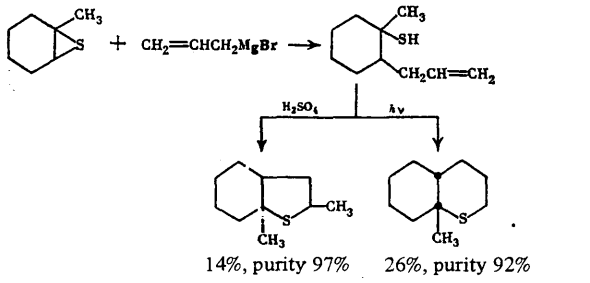
2-Allylcyclopentanethiol has been obtained from cyclopentene sulphide and allyl-magnesium bromide.[77] Its cyclisation on UV irradiation affords 2-thiabicyclo-[4.3.0]-nonane with an admixture of 3-methyl-2-thiabicyclo[3.3.0]-octane (ratio 97:3, overall yield 42%). In cyclisation on treatment with sulphuric acid, the ratio of these structural isomers is reversed, but the overall yield of thiabicycloalkanes is low (13%). The authors explained this by the difficulty of the formation of two *trans*-joined five-membered rings:[78]



It has been shown[79] that 2-(α-methyl-β-propenyl)cyclohexanethiol is formed from cyclohexene sulphide and crotylmagnesium bromide, which reacts in the form of 3-magnesiobromobut-1-ene; its cyclisation on irradiation gives rise to a mixture of 8,9-dimethyl-7-thiabicyclo[4.3.0]nonane (2,3-dimethyl-1-thiahydrindan) and 5-methyl-2-thiabicyclo[4.4.0]-decane (4-methyl-1-thiadecalin) in an overall yield of 50%; cyclisation on treatment with sulphuric acid results in the selective formation of a thiahydrindan derivative. In both procedures the cyclisation is non-stereospecific. The pure structural isomers are obtained with the aid of GLC.



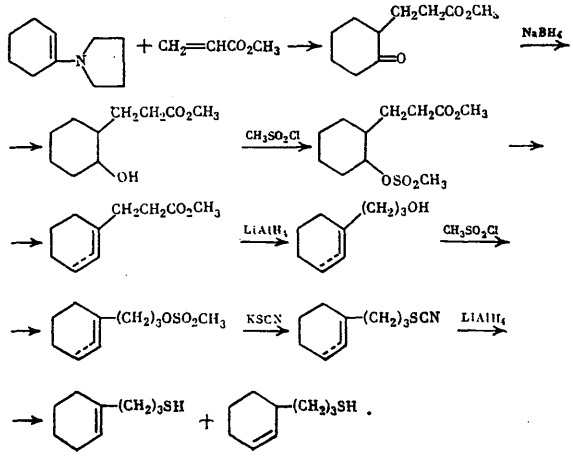
When 1-methylcyclohexene sulphide reacts with alkylmagnesium bromide, the C–S bond at the carbon atom attached to the larger number of hydrogen atoms is broken; the cyclisation of the thiol leads to thiabicycloalkanes with the methyl substituent at the ring junction in the *trans*-position relative to the angular hydrogen atom—6,8-dimethyl-7-thiabicyclo[4.3.0]nonane (2,8-dimethyl-1-thiahydrindan) and 1-methyl-2-thiabicyclo[4.4.0]decane (9-methyl-1-thiadecalin).[80] Although the yields are low for both cyclisation procedures, the processes are fairly selective. The subsequent purification via mercury complexes makes it possible to obtain "chromatographically pure" thiabicycloalkanes:



Fairly pure 8-methyl-7-thiabicyclo[4.2.0]nonane (2-methyl-1-thiahydrindan)[81] and 2-thiabicyclo[4.4.0]decane (1-thiadecalin)[41,81] have also been obtained in 52 and 67% yields from cyclohexene sulphide and allylmagnesium bromide; they were previously synthesised by another method.[19,82]

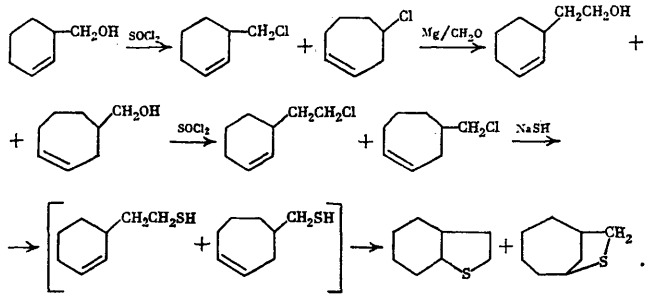
Claus and Vierhapper[83] used azobisisobutyronitrile for the radical cyclisation of *trans*-allyl cyclohexanethiols (cf. Kondo and Negishi[41]). 2-Thiabicyclo[4.4.0]decanes are then formed preferentially. With the aid of this initiator, 4-, 7-, and 10-methyl-*trans*-2-thiabicyclo[4.4.0]decanes were obtained for the first time. The same authors synthesised 4-, 6-, 8-, and 10-methyl-*cis*-2-thiabicyclo[4.4.0]decanes[83] using the fact that the radical cyclisation of 3-mercaptopropylcyclohexenes under the influence of the same initiator proceeds preferentially with formation of *cis*-joined thiabicyclodecanes.

The syntheses of such mercaptans are extremely laborious—for example a mixture of 1- and 3-(3-mercaptopropyl)cyclohexenes, cyclisation leads to *cis*-2-thiabicyclo[4.4.0]decanes, is obtained from pyrrolidinocyclohexene in 8 stages:



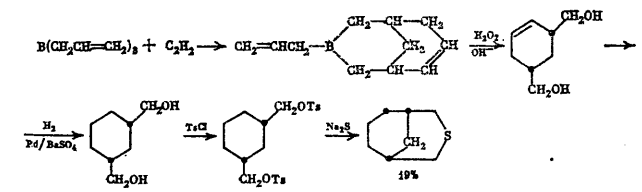
The content of *cis*-2-thiabicyclo[4.4.0]decane in the mixture after the cyclisation of there mercaptans is 68%. It is isolated by separating the complexes with mercury(II) chloride or by preparative GLC; methyl-*cis*-2-thiabicyclo[4.4.0]-decane has been obtained[83] using analogous schemes. The configurations and conformations of the compounds synthesised were identified[84] by means of ^1H and ^{13}C NMR spectroscopy.

Four unsubstituted bridged thiabicyclononanes have been synthesised. *cis*-7-Thiabicyclo[4.2.1]nonane mixed with *cis*-7-thiabicyclo[4.3.0]nonane (*cis*-1-thiahydrindan) was obtained[85] from 3-hydroxymethylcyclohexene according to the scheme

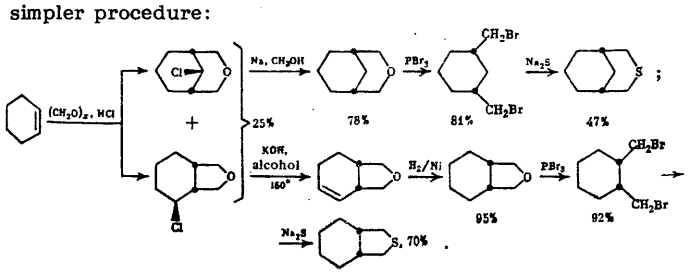


The formation of a mixture of such sulphides is a result of ring expansion on chlorination of hydroxymethylcyclohexene and also the cyclisation of thiols only at the nearest (relative to the substituent) end of the double bond. The overall yield of the mixture of sulphides in the last stage of the scheme is 90% and they are formed in approximately equal amounts; the mixture is separated by preparative GLC.

7-Thiabicyclo[3.3.1]nonane has been synthesised; its precursor—1,3-di(hydroxymethyl)cyclohexane—was obtained from acetylene and triallylborane:[86]



The same sulphide has been recently synthesised[87] by a simpler procedure:

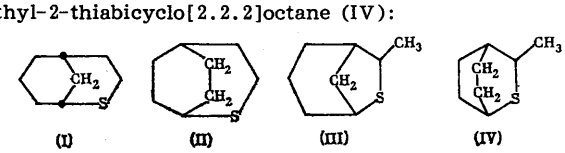


The second, isomeric chloromethylation product "was not wasted"—the authors used it to synthesise 8-thiabicyclo-[4.3.0]nonane, which had been previously obtained by Birch et al.[88] by a procedure involving a greater number of stages.

A two-stage method has been proposed for the synthesis of bridged thiabicyclooctanes and thiabicyclononanes from vinylcyclohexenes.[89,90] When vinylcyclohexenes interact with sulphur dichloride, intramolecular cyclisation adducts, namely isomeric dichlorothiabicycloalkanes, are formed (together with oligomeric products). The adducts are subjected to reductive dechlorination whereupon mixtures of thiabicycloalkanes are formed and are then resolved by preparative GLC.

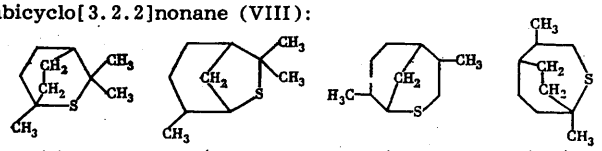
In the course of the exchange of chlorine atoms for hydrogen, skeletal isomerisation takes place, the extent of which depends on the presence of methyl groups in the vinylcyclohexenes, their positions, the nature of the reducing agent, and the reduction conditions.

Unsubstituted thiabicycloalkanes have been obtained[89] from 4-vinylcyclohexene and sulphur dichloride on reduction by diisobutylaluminium (the yield of their mixture was 23%): 2-thiabicyclo[3.3.1]nonane (I) and 2-thiabicyclo[3.2.2]-nonane (II), and also methyl-substituted derivatives: *exo*- and *endo*-7-methyl-6-thiabicyclo[3.2.1]octanes (III) and 3-methyl-2-thiabicyclo[2.2.2]octane (IV):



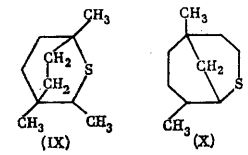
(I) (II) (III) (IV)

A mixture of thiabicycloalkanes (its yield was 86% after reductive dechlorination) has been synthesised analogously from 4-isopropenyl-1-methylcyclohexene.[90] 1,3,3-Dimethyl-2-thiabicyclo[2.2.0]octane (V), 4,7,7-trimethyl-6-thiacyclo-[3.2.1]—octane (VI), 4,8-dimethyl-2-thiabicyclo[3.3.1]-nonane (VII), and its epimer were isolated; the reduction of the adduct with sodium tetrahydroborate results in the formation also of considerable amounts of 1,4-dimethyl-2-thiabicyclo[3.2.2]nonane (VIII):



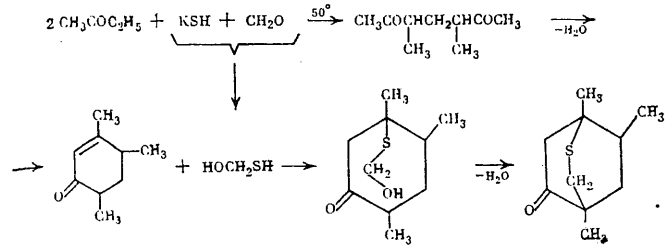
(V) (VI) (VII) (VIII)

After the reduction of the adducts of sulphur dichloride and 1,4-dimethyl-4-vinyl-1-cyclohexene with diisobutyl-aluminium, a mixture of 1,3,4-trimethyl-2-thiabicyclo[2.2.2]-octane (IX) and 5,8-dimethyl-2-thiabicyclo[3.3.1]nonane (X) was obtained in proportions of 3:1 in 19% yield:



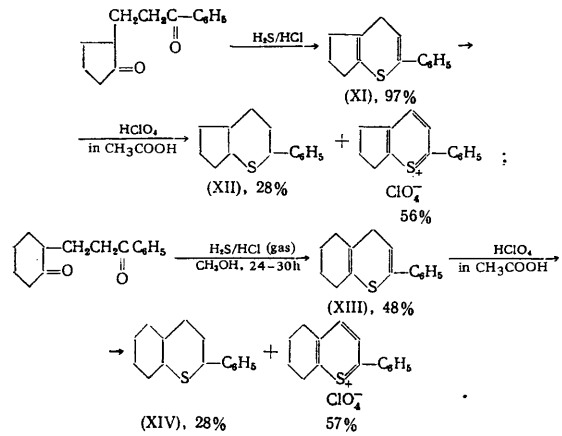
(IX) (X)

The thioalkylation of ethyl methyl ketone[91] makes it possible to obtain extremely simply (in one stage) 1,4,5-trimethyl-7-thiabicyclo[2.2.2]octan-2-one in 20% yield (the remainder consists of polymeric products):

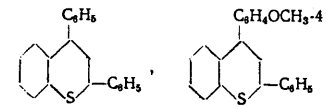


During the 1970's, the interaction of "semicyclic" 1,5-diketones with hydrogen sulphide in the presence of protic acids was investigated. The initial 1,5-diketones are obtained by the Michael reaction from cyclopentanone and arylideneacetophenones.[92] The reaction of diketones with hydrogen sulphide proceeds at room temperature. Aryl-substituted polymethylene-4*H*-thiapyrans are formed and in the presence of strong acids disproportionate to a mixture of polymethylenethiopyrylium salts and arylthiabicycloalkanes.[93] The latter are formed in low yields (of the order of 30%). However, the ease of their isolation from the mixture (readily separated from thiopyrylium salts by extraction with ethylhexane) makes up for this disadvantage.

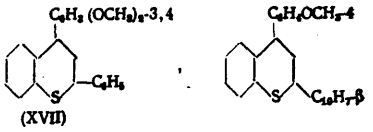
Aryl-2-thiabicyclo[4.3.0]nonanes are obtained from cyclopentanone derivatives and aryl-2-thiabicyclo[4.4.0]decanes are synthesised from cyclohexanol derivatives, for example:[94]



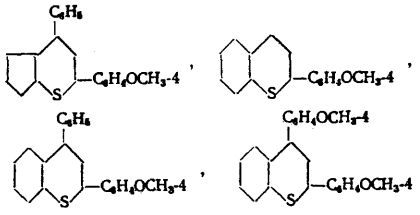
The compounds



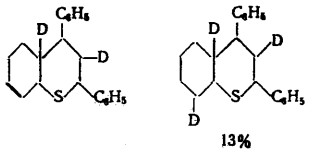
(XV) (XVI)


(XVII)

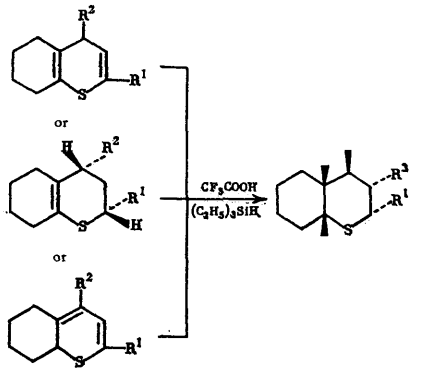
have been obtained in the same way.[92,94] Compounds (XII) and (XIV)–(XVII) as well as other thiabicycloalkanes have been synthesised[95] in accordance with an analogous scheme from the corresponding 1,5-diketones and hydrogen sulphide, but in this case the reaction was in trifluoroacetic acid:



The study of the reaction of polymethylene-4*H*-thiopyrans with deuteriotrifluoroacetic acid[96] made it possible to establish the site of protonation in the disproportionation reaction; di- and tri-deuterio-3,5-diphenyl-2-thiabicyclo[4.4.0]decanes were then obtained for the first time:

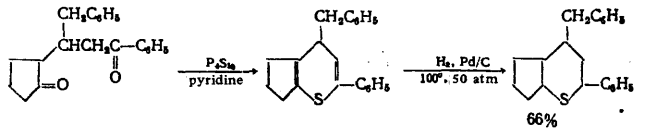

13%

Aryl-2-thiabicycloalkanes have been obtained in high yields by the catalytic hydrogenation (over Pd/C) of the corresponding 4*H*-thiopyrans, such as, for example, compounds (XI) and (XIII).[97] Compounds (XIV)–(XVII) have also been obtained by the ionic hydrogenation of condensed dihydro-4*H*- and dihydro-6*H*-thiopyrans (the yields were respectively 61, 60, 59, and 27%).[98] Regardless of the position of the double bond in the initial heterocycle and the degree of unsaturation, the *cis*, *cis*, *cis*-isomers are then formed:

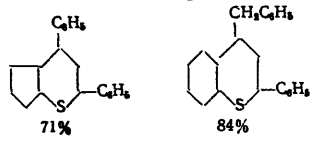


Compound (XV), obtained in 25% yield by the disproportionation of the corresponding thiopyran derivative, also has the *cis*,*cis*,*cis*-configuration.[99]

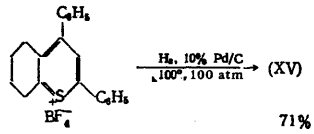
The initial condensed 4*H*-thiopyrans have also been synthesised from 1,5-diketones and P_4S_{10} by Kupranets's procedure,[92] for example:


66%

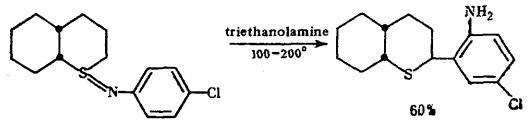
Compounds (XII) and (XIV)–(XVII) as well as thiabicycloalkanes have been obtained analogously:[97,100]


71% 84%

Hydrogenation of salts derived from arylthiochromylium also leads to thiabicycloalkanes:[52]

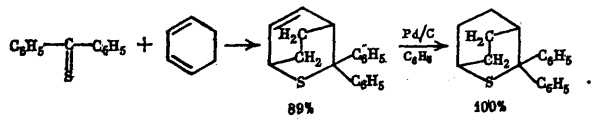

71%

3-(2-Amino-5-chlorophenyl)-2-thiabicyclo[4.4.0]decanes can be obtained by the rearrangement of sulphimides—2-(*p*-chlorophenylimino)-2-thiabicyclo[4.4.0]decanes.[101] The synthesis and stereochemistry of the formation of the latter has been examined in detail in a review:[93]


60%

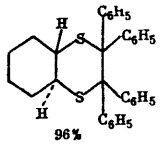
The product of the rearrangement is isolated by chromatography. The yields of the products of the rearrangement of sulphimides derived from methyl-2-thiabicyclo[4.4.0]decanes are 16–71% (depending on the conformation of the initial compound). If there is no steric hindrance, the rearrangement proceeds with a high degree of stereospecificity (>95%): shlphimides with an equatorial or axial S–N bond afford products with an equatorial or axial aryl substituent respectively.

The initial compound for the synthesis of αα-disubstituted (relative to the sulphur atom) thiabicycloalkanes may be thiobenzophenone: its condensation with cyclohexa-1,3-diene led to the formation of 3,3-diphenyl-2-thiabicyclo-[2.2.0]oct-5-ene which was then hydrogenated:[47]


89% 100%

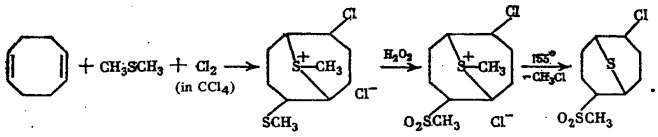
trans-2-Thiabicyclo[4.4.0]decan-5-one has been obtained in 50% yield from 1-(3-dimethylaminopropanoyl)cyclohexene and hydrogen sulphide in the presence of sodium acetate; the analogous reaction with 1-(3-dimethylaminobutanoyl)cyclohexene leads to the 3-methyl derivative in 78% yield.[102] These compounds can also be obtained from the methiodides of the above bases and sodium sulphide.[55,93]

A review[103] devoted to the photocycloaddition of carbonyl compounds of olefins quotes the reaction of thiobenzophenone with cyclohexene which resulted in the formation of 3,3,4,4-tetraphenyl-2,5-dithiabicyclo[4.4.0]decane with a *trans*-junction between the rings:

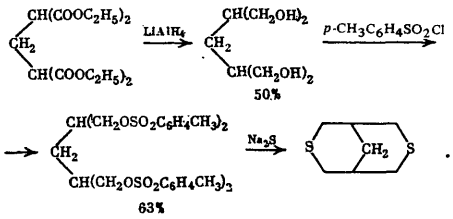


96%

The synthesis of pesticides based on 2-chloro-6-methanesulphonyl-9-thiabicyclo[3.3.1]nonane has been patented;[104] the nonane derivative was synthesised from cycloocta-1,5-diene and dimethyl sulphide in accordance with the scheme



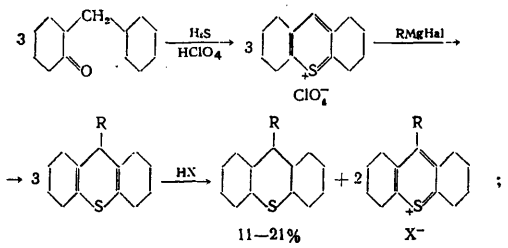
3,7-Dithiabicyclo[3.3.1]nonane has been synthesised[105] using the scheme



2. Thiatricycloalkanes

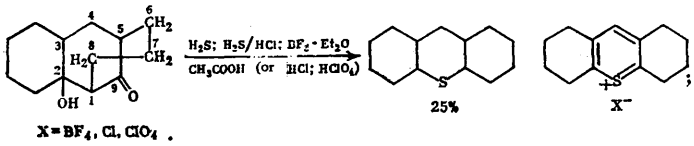
The synthesis of thiapolycycloalkanes with the aim of modelling the sulphur compounds in petroleum has acquired special importance in connection with the more extensive investigation of the composition and properties of the high-molecular-weight component of petroleum. However, in contrast to the syntheses of the thiamonocyclo- and thiabicycloalkanes, the methods of synthesis of thiapolycycloalkanes have developed little in recent years. This is apparently associated with the difficulty of constructing their bicyclic or tricyclic precursors.

The synthesis of perhydrothioxanthene from cyclohexylidenecyclohexanone has been examined in a monograph;[19] 9-substituted perhydrothioxanthenes have been obtained using the same scheme:[106,107]



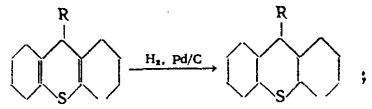
R=C_2H_5, C_3H_7, C_6H_5, X=ClO_4, $FeCl_4$, Cl, CF_3COO, Br.

Perhydrothioxanthene has also been obtained from 2-hydroxy-2,3-tetramethylenebicyclo[3.3.1]nonan-9-one:[108]



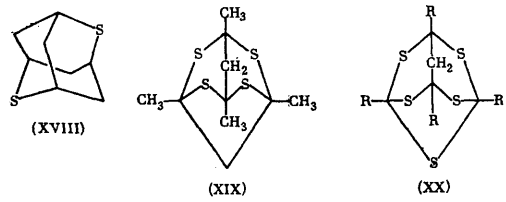
X=BF_4, Cl, ClO_4.

Perhydrothioxanthenes can be obtained in satisfactory yields by the catalytic hydrogenation of thioxanthylium salts[52] and also octahydrothioxanthenes:[97]



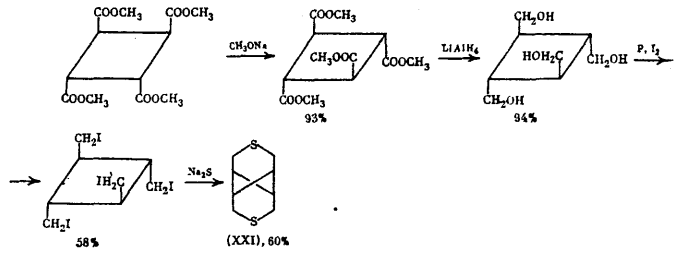
R=H, CH_3.

The syntheses of 2,6-dithiaadamantane (XVIII) from thiabicyclo[3.3.1]nona-2,6-diene, of tetrathiaadamantane (XIX) from dithioacetylacetone, and of tetrathiaadamantane, pentathiaadamantane (XX), and hexathiaadamantanes from β-dicarbonyl compounds and thioacetic acid have been considered in a review:[109]



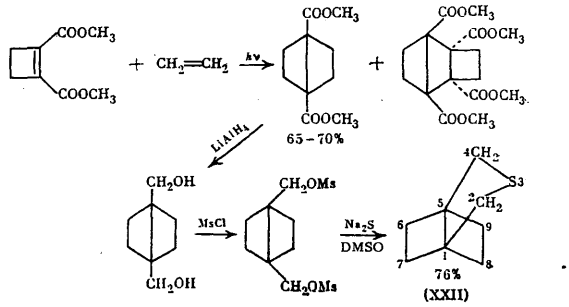
(XVIII) (XIX) (XX)

4,9-Dithiatricyclo[4.4.0.$0^{2,7}$]decane (XXI) has been synthesised by a comparatively simple procedure.[110] The photodimerisation of dimethyl fumarate in the solid phase yielded tetramethoxycarbonylcyclobutane and from the latter *trans*, *trans*, *trans*,-1,2,3,4-tetra(iodomethyl)cyclobutane was obtained. Sodium sulphide is added into its solution in absolute ethanol with the aid of the Soxhlet apparatus and the sulphide (XXI) is obtained:

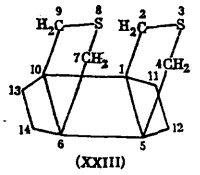


A characteristic feature of the structure of the sulphide (XXI) is the flattening of the six-membered ring. It is of interest that there is a maximum at 246 nm in its UV spectrum. The authors[110] explain this by the result of the interaction of the σ-orbitals of the four-membered ring and the *p* electrons of the sulphur atom.

3-Thiatricyclo[3.2.2.$0^{1,5}$]nonane or 3-thia[3.2.2]propellane (XXII) has been synthesised[111] by the photochemical cycloaddition of ethylene to 1,2-dimethoxycarbonylcyclobutene:

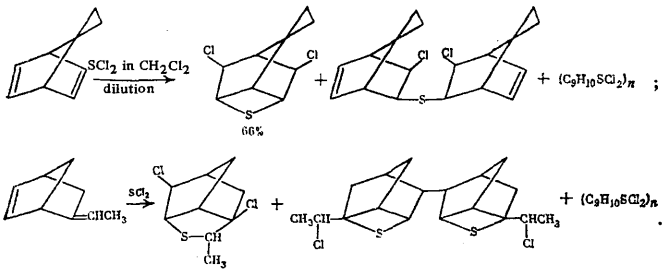


The pentacyclic sulphide (XXIII) was obtained[111] from the photodimer, formed in the first stage of the synthesis, via the same sequence of reactions; its yield in the last stage of the synthesis was 64%:



(XXIII)

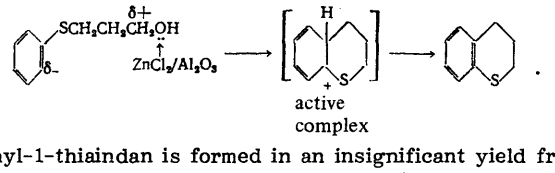
Adducts, consisting of chloro-derivatives of saturated tricyclic sulphides with a thiaskeletal structure have been obtained from bicyclic dienes and sulphur dichloride:[112]



3. Semiaromatic Sulphides

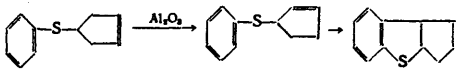
The advances in the synthesis of "semiaromatic" polycyclic sulphides (i.e. those where at least one CH_2 group adjoins the sulphur atom in the ring) have been associated in recent years with the study of the [3,3]sigmatropic ("thio-Claisen") rearrangement of alkenyl aryl sulphides and principally with the development of the syntheses of thiacyclophanes.

The reactions of alkenyl aryl sulphide and also certain thiophenols were carried out in the presence of acid catalysts.[113–116] This resulted in the formation of thiaindans and thiachromans. Thus, when 1-phenylthio-3-propanol is passed at 300 °C over alumina on which zinc chloride has been deposited, thiachroman is formed (31–35%):[113,115]



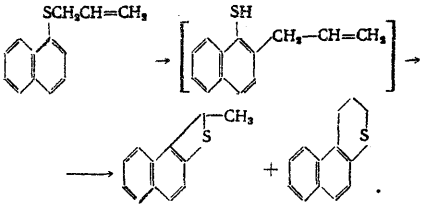
active complex

2-Methyl-1-thiaindan is formed in an insignificant yield from allyl phenyl sulphide over this catalyst, while over alumina, which is a less acid catalyst, the yield is better (33%).[114] Under these conditions, thiaindans are partly dehydrogenated to thiaindenes (in the presence of zeolite, the overall yield of 2-methyl-2-thiaindan and 2-methylthiaindene is 47%.[115]) The reaction of but-3-enyl phenyl sulphide in the presence of 20% $ZnCl_2/Al_2O_3$ at 30 °C takes place with formation of 33% of 4-methylthiochroman.[116] The formation of 15% of a tricyclic "semiaromatic" sulphide, namely cyclopentano-2,3-dihydrobenzothiophen, from cyclopentenyl phenyl sulphide has been noted:[116]

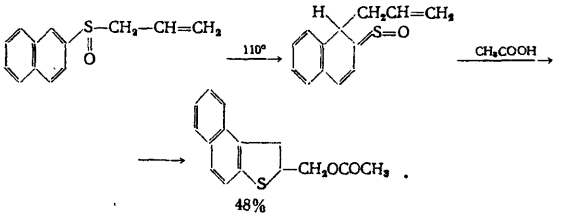


The catalytic synthesis of such semiaromatic sulphides from alkenyl phenyl sulphides is attractive by virtue of its simplicity but in the communications considered only the contents of the sulphide in the catalytic reaction mixture, determined by GLC analysis, are given, while the yields of the individual derivatives of thiaindans and thiachromans are not indicated.

The "thio-Claisen" rearrangement has continued to be extended to new objects under traditional conditions—with heating in the absence of a solvent or in aprotic solvents. Heating of allyl 1-naphthyl sulphide at 190 °C in quinoline leads to the formation of a mixture of approximately equal amounts (59:41) of tricyclic derivatives of thiaindan and thiachroman:[117]

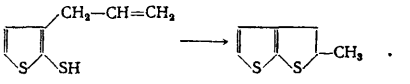


Japanese investigators[118] heated allyl 2-naphthyl sulphoxide in the presence of acetic acid and dimethylformamide and obtained a functional derivative of a tricyclic semiaromatic sulphide:

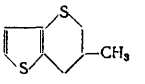


48%

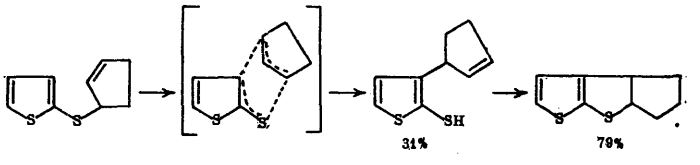
Semiaromatic sulphides have also been synthesised from thiophen derivatives.[119–121] In this case too mixtures of dihydrothiolen and dihydrothiopyran are usually formed. The synthesis where only one of the possible structural isomers is formed are of preparative interest. Thus, when 3-allylthiophen-2-thiol is heated in hexamethylphosphoramide, only 2-methyl-2,3-dihydrothieno[2,3b]thiophen is formed in 50% yield:[119]



The thermal rearrangement of β-methylallyl 3-thienyl sulphide leads to only 3-methylthieno[3,2*b*]dihydrothiopyran:[119]

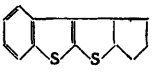


3-(Cyclopent-2-enyl)-thiophen-2-thiol cyclises at 120 °C in quinoline with formation of cyclopentano-2,3-dihydrothieno-[2,3*b*]thiophen; the initial thiol is obtained beforehand from cyclopent-2-enyl 2-thienyl sulphide:[120]



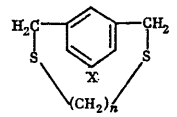
31% 79%

The corresponding thiol is obtained analogously in a low yield (12–14%) from cyclopent-2-enyl 2-benzothienyl sulphide and its cyclisation affords cyclopentano-2,3-dihydrobenzothieno[2,3*b*]thiophen:[121]



The synthesis of cyclophanes—cyclic compounds containing one or several benzene rings joined by polymethylene bridges in the *o*-, *m*-, or *p*-positions—has developed in recent years. These compounds serve as convenient objects for the study of a large number of problems in theoretical organic chemistry. Thiacyclophanes usually serve as precursors of cyclophanes, being converted into the latter, for example, with the aid of the Stevens rearrangement. The methods of synthesis of thiacyclophanes have been considered in detail in two reviews.[69,70]

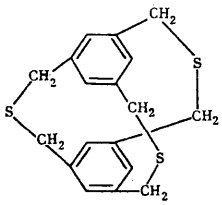
A general method of synthesis of thiacyclophanes involves the reaction of the corresponding dibromo-derivatives with dithiols. For example, more than 100 dithia-*meta*-cyclophanes have been synthesised and investigated in two studies,[69,122] for example, compounds of the type



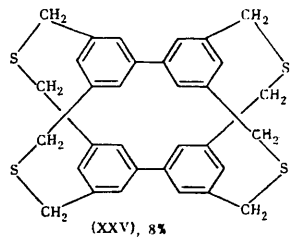
n = 2–10, X=H,F,Cl,Br,CH$_3$,CH$_3$O,CN

They were obtained by the reaction of equimolar amounts of αω-bismercaptans with the corresponding αα′-dibromo-*m*-xylenes in a basic medium (yields 3–90%). High dilution is used in the synthesis of thiacyclophanes of medium size.[123]

The precursors of two- and three-layer cyclophanes (also referred to as "cage compounds") are bridged polythiacyclophanes, for example, compounds (XXIV) and (XXV):

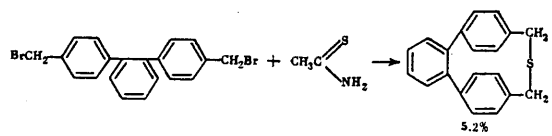


(XXIV), 12%

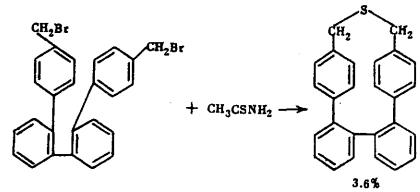


(XXV), 8%

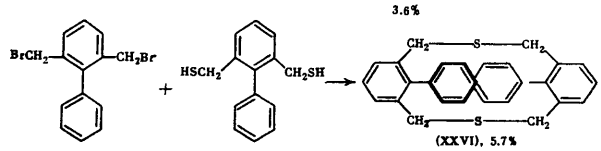
Compound (XXIV) has been synthesised by Boekelheide and Hollings[124] and compound (XXV) by Vögtle et al.[125] Strained thiscyclophanes were synthesised subsequently[126] using the so called "caesium effect", which consists in the fact that the cyclocondensation of the dibromo-derivatives with thioacetamide or with 2,6-di-(mercaptomethyl)biphenyl takes place only in the presence of equimolecular amounts of caesium ions (in the form of Cs_2CO_3 in DMF); the yields of the required products are however low.



5.2%



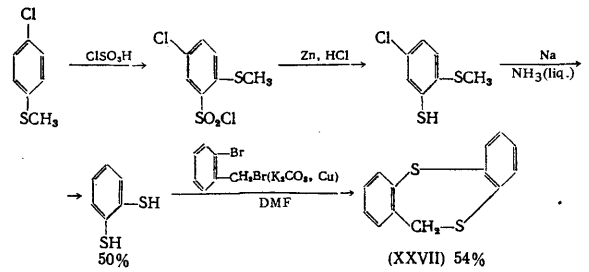
3.6%



(XXVI), 5.7%

Compound (XXVI) is a mixture of the *syn*- and *anti*-stereoisomers which are separated by chromatography on silica gel.

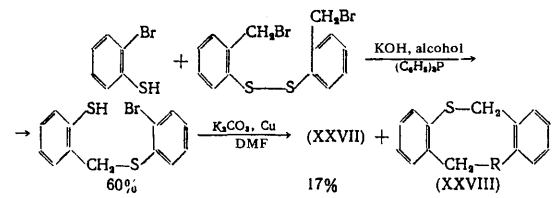
In order to obtain substances with psychotropic (antidepressant) activity, Czech investigators[127] synthesised derivatives of dithiacyclophanes—11*H*-debenzo[b,e]-1,4-dithiepin (XXVII); the starting compound was 4-chlorothioanisole:



50%

(XXVII) 54%

If the synthesis of compound (XXVII) was begun with 2-bromothiophenol, then another dithiacyclophane, namely 6*H*,12*H*-dibenzo[*b*,*f*]-1,5-dithiocin (XXVIII), was obtained together with compound XXVII):

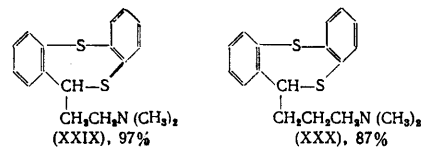


60%

17%

(XXVIII)

By treating compound (XXVII) with butyl-lithium and 2-dimethylaminoethyl or 3-dimethylaminopropyl chloride, the dithiacyclophanes (XXIX) and (XXX) were obtained respectively (the pure compounds were obtained in the form of the oxalates); they were found to exhibit antireserpine activity:

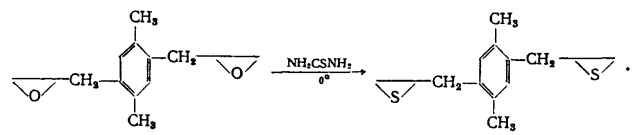


(XXIX), 97%

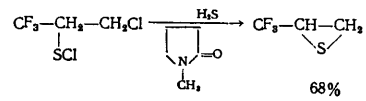
(XXX), 87%

The most important studies published during the preparation of the review for print are examined below.

Unsubstituted acetylthiirans and 2- and 3-methylacetylthiirans have been obtained in 70–80% yields from acetyloxirans.[128] The latter are converted into diethylketals, which are treated with thiourea and then hydrolysed. The oxygen is readily replaced by sulphur in the symmetrical dioxiran:[129]

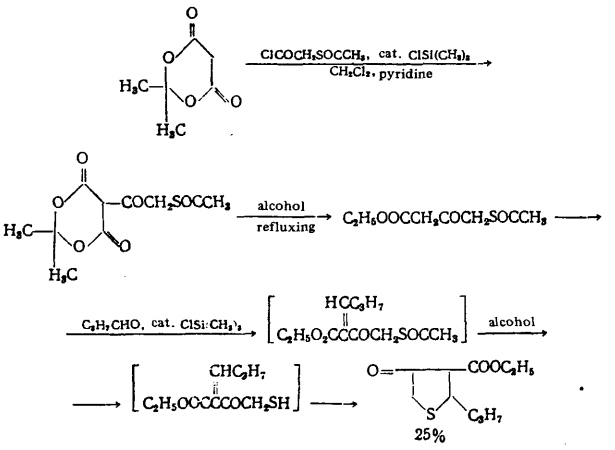


Trifluoromethylthiiran has been obtained[130] from chloropropane-2-sulphenyl chloride and hydrogen sulphide:

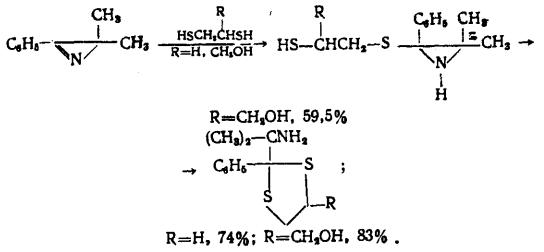


68%

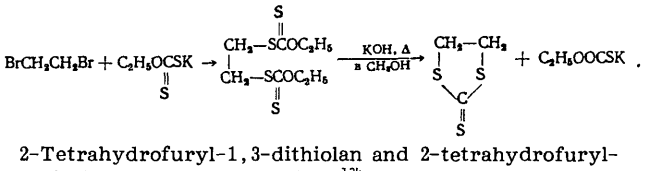
Polyfunctional derivatives of thiolan have been synthesised[131] using Meldrum's acid, for example:



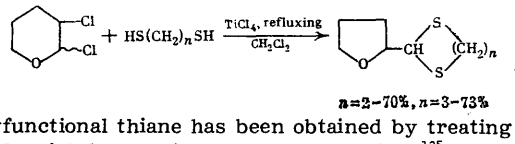
2-Aminoalkylated derivatives of 1,3-dithiolan have been synthesised from β-dithiols and 2*H*-azirines:[132]



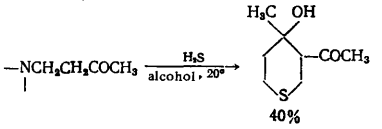
A preparative method of synthesis of 1,3-dithiolan-2-thione and 4-phenyl-1,3-dithiolan-2-thione from dibromoethane and 1,2-dibromo-1-phenylethane and xanthate has been described:[133]



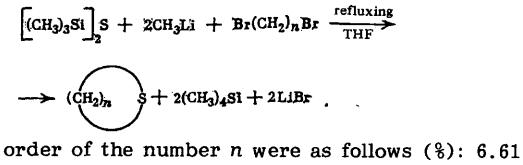
2-Tetrahydrofuryl-1,3-dithiolan and 2-tetrahydrofuryl-1,3-dithiane have been obtained[134] from dithiols and 2,3-dichlorotetrahydropyran:



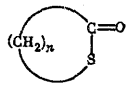
A polyfunctional thiane has been obtained by treating ketonic Mannich bases with hydrogen sulphide:[135]



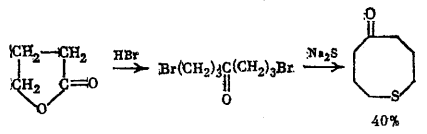
Sulphides containing more than six members in the ring have been synthesised[136] using the reactive form of Li_2S (at the instant of formation) in accordance with the scheme:



The yields in order of the number *n* were as follows (%): 6.61, 7.34, 8.22, 9.15, 10.20, and 12.31. The macrocyclic thiolactones

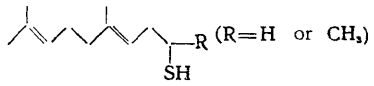


have also been obtained by reaction with $Br(CH_2)COCl$. The yields of the thiolactones in order of the number *n* were as follows (%): 5.73, 7.0, 11.47, and 15.64. 5-Cyclothiaoctanone has been synthesised[137] from γ-butyrolactone:[137]

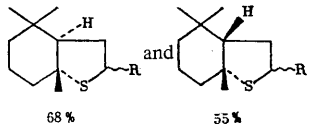


cis,cis-5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane has been synthesised[138] in 55% yield by treating specially obtained 2-thieten with tetracyanoethylene.

Cyclisation of the stereoisomers of the homogeranioIthiols

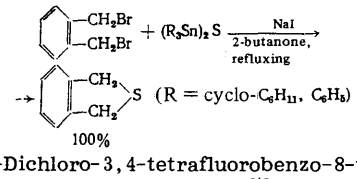


with the aid of boron trifluoride/etherate[139] the *trans*- and *cis*-*gem*-dimethyl- and the *trans*- and *cis*-trimethyl-thiahydrindans respectively; the method makes it possible to control only the stereochemistry of the ring junction:

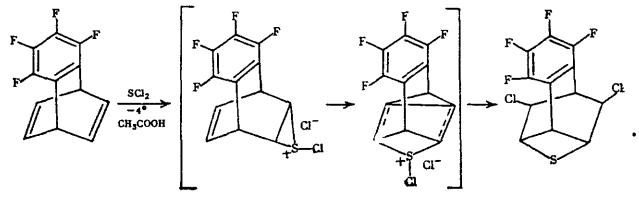


The thio-Claisen rearrangement has been extended[140] to alkenylthiotropones.

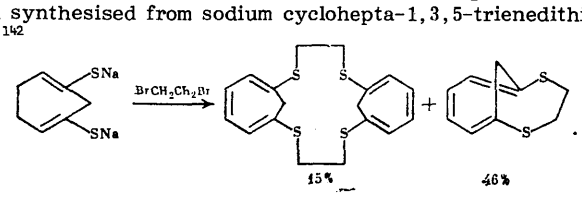
1,3-Dihydroisothionaphthene has been obtained[136] using organotin compounds:



exo-exo 6,9-Dichloro-3,4-tetrafluorobenzo-8-thiatricyclo-[3.3.1.$0^{2,7}$]nonene has been obtained[141] by means of the scheme



A thiocrown ether with a cycloheptatriene fragment has been synthesised from sodium cyclohepta-1,3,5-trienedithiolate:[142]



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